California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE DETERMINATION OF C_2 TO C_{12} HYDROCARBONS IN AUTOMOTIVE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

Standard Operating Procedure No. MLD 102 / 103
Revision 2.0

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SOP No. 102/103 - PROCEDURE FOR THE DETERMINATION OF C2 TO C12 HYDROCARBONSIN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

1 Introduction

1.1 This document describes a method of analyzing, by gas chromatography (GC), C_2 to C_5 (light-end) hydrocarbons and C_6 to C_{12} (mid-range) hydrocarbons, in the range of 20 to 10000 parts per billion carbon (ppbC), from automotive source samples. It is derived from the Air Resources Board Methods 1002 and 1003 (Ref. 9.1). This method does not include sample collection procedures.

2 Method Summary

2.1 This procedure uses two gas chromatographs (GCs), one (the light-end GC) for analyzing C_2 to C_5 hydrocarbons and the other (the mid-range GC) for analyzing C_6 to C_{12} hydrocarbons, each with its own automated cryogenic preconcentration system (cryotrap).

2.2 For routine motor vehicle exhaust testing, the vehicle is tested according to the Federal Test Procedure (FTP, Ref. 9.2), using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust for sampling.

2.3 Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs, Ref. 9.2), gas standard cylinders or canisters, and hydrocarbon-containing samples from other miscellaneous sources.

2.4 The samples are received by the laboratory in Tedlar bags or in stainless steel canisters. The sample is injected into the GC by means of the automatic gas phase sampling valve system. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The flame ionization detector (FID) is used for detection and quantification.

2.5 The hydrocarbon concentrations are determined by integrating the peak areas and using response factors determined from National Institute of Standards and Technology (NIST)-traceable standards during calibration.

2.6 The computerized GC data acquisition system identifies the hydrocarbon associated with each chromatographic peak (Ref. 9.3)

3 Interferences and Limitations

3.1 Any component (e.g., Freon group, Tedlar bag contaminants) present in the sample having a retention time similar to that of any hydrocarbon being measured is an interferent. Therefore, proof of chemical identity requires confirmation by other methods and instrumentation, e.g., gas chromatography/mass spectrometry (GC/MS).

3.2 To maximize sample integrity, sample bags should not leak or be exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid reactions due to reactive hydrocarbons. The compound 1,3-butadiene (a light-end hydrocarbon), most of which is in cold-start exhaust test bag no. 1, is unstable. Therefore, all cold-start bag no. 1 samples must be analyzed for the light-end hydrocarbons within 8 hours. Cold-start bag no. 2, bag no. 3 and background must be analyzed within 24 hours, although analysis within 8 hours is recommended.

3.3 The light-end analysis is calibrated with propane. The propane response factor is used for all light-end hydrocarbons. This procedure will introduce an error if the propane response is not representative of the responses of all other light-end compounds.

3.4 The mid-range analysis is calibrated with benzene or propane (Section 5.2.2.1). The benzene (or propane) response factor is used for all mid-range hydrocarbons and ethers, such as MTBE. This procedure will introduce an error if the benzene (or propane) response is not representative of the responses of all other mid-range compounds.

4 Instrumentation and Apparatus

4.1 Tedlar bags, 2 mils in thickness, nominally 5 to 10 liters in capacity and equipped with Swagelok QuikConnect fittings, are used to contain the samples from the dyno test facility.

4.2 Two gas chromatographs, VARIAN 3400 or 3600 or equivalent, equipped with gas sampling valve systems (as described in Ref. 9.3) and FIDs, are connected together by their sampling lines and electronic start signals.

4.3 The light-end GC uses an analytical column, Al203/KCl PLOT [50 meters (m) x 0.32 millimeters (mm) inner diameter (ID)] and, to prevent water damage to the PLOT column, a Carbowax WCOT (25 m x 0.53 mm ID) precolumn; the mid-range GC uses a DB-1 WCOT analytical column [40 m x 0.18 mm ID with a 0.4 micron (u) film thickness or 60 m x 0.32 mm ID with a 1 u film thickness]. Precolumns and analytical columns are purchased from CHROMPACK, Inc., J&W or equivalent.

4.4 A cryotrap of nickel tubing [10" x 1/16" outer diameter (OD), 0.040" ID] is used to concentrate the sample.

4.5 A PC-based data acquisition system (Varian Star or equivalent) is used to quantitate peak areas.

5 Reagents and Materials

5.1 Gases used to support the GC analysis shall be of the following purities:

5.1.1 Helium shall have a minimum purity of 99.9999% and pass through a molecular sieve trap to ensure purity before entering the GC system.

5.1.2 Hydrogen shall have a minimum purity of 99.999%.

5.1.3 Zero nitrogen shall have a minimum purity of 99.998%.

5.1.4 Ultra-zero air shall have less than 0.1 part per million (ppm) hydrocarbon (as methane).

5.2 Gas standards with concentrations in the range of 100 to 10000 ppbC are used for daily calibration, daily quality control and linearity/limit of detection (LOD) determinations.

5.2.1 Primary calibration gas standards, purchased from NIST, are used to verify the concentrations of working standards used for daily calibration.

5.2.2 The working standard is purchased from Scott Specialty or other vendor.

5.2.2.1 The working calibration standard contains at least propane (approximately 3000 ppbC) for the light-end calibration analysis and benzene (approximately 1500 ppbC) for the mid-range calibration analysis.

5.2.2.2 If propane is shown to have a mid-range response factor that is representative of a broad range of mid-range compounds, propane may be used to calibrate both the light-end and mid-range analyses. In that case, the calibration standard would be required to contain only propane.

5.2.2.3 The concentration(s) of the calibration compound(s) is verified ($\pm$ 2%) by comparison with the NIST standard(s).

5.2.2.3 Additional compounds may be included in the calibration standard for response factor comparisons, retention time confirmations, etc, if desired.

5.2.3 The quality control gas mixture is also purchased from Scott Specialty or other vendor.

5.2.3.1 It contains at least the following gases: ethene, propane, n-butane, and 2-methylpropene for the light end analysis (Ref. 9.1, Method 1002, Section 5.6) and n-hexane, n-octane, n-decane, benzene, toluene, and m- or p-xylene for the mid-range analysis (Ref .9.1, Method 1003, Section 5.6).

5.2.3.2 These ten compounds are monitored for quality control purposes (Section 8).

5.2.3.3 Additional compounds may be included in the control standard for response factor comparisons, retention time verifications, etc., if desired.

5.2.4 Table 1 shows the composition of the calibration and control standard gases in use at this date.

5.2.5 Figures 1 through 4 show the light-end and mid-range chromatograms of the current calibration standards.

5.4 Liquid nitrogen (LN2) is used to cool the cryogenic traps and column ovens.

6 Procedure

6.1 The operating conditions for the gas chromatographs are given in Table 2.

6.1.1 Each GC pair may have some deviation of these conditions to optimize the operation.

6.2 Samples in Tedlar bags (or stainless steel canisters) are attached to the gas phase autosampling valve system and simultaneously drawn through a fixed-volume sample loop in the light-end GC and through another fixed sample loop in the mid-range GC, with a vacuum pump [variable, usually at about 300 mL/min for 2 minutes (variable)]. The volume of the sample loop may vary for each GC, depending on its intended use. For the light-end GC it is usually 10 milliliters (mL), nominal, and for the mid-range GC it varies from 7 to 30 mL

.

6.3 For the light-end GC the sample is eluted through the precolumn and loaded into the cryotrap; for the mid-range GC the sample is loaded directly into the cryotrap.

6.4 After all the light-end hydrocarbons are eluted through the precolumn, the light-end GC precolumn is back flushed to prevent the heavy hydrocarbons and water from eluting onto the analytical (PLOT) column. Helium is flushed backward through the precolumn out to vent. The cryotraps for both GCs are isolated and heated.

6.5 When the cryotrap is heated for a specific time (corresponding to $200^{o}C$), the isolation valve is opened and the samples are injected into the analytical column of each GC.

6.6 As each separated hydrocarbon elutes from the column through the FID, a signal response (peak) is generated and recorded by the data system.

6.7 The data system generates separate light-end and mid-range reports, each containing the chromatograms and peak identifications and corresponding concentrations.

6.7 The peak identifications and peak concentrations determined by the data system are reviewed and, if necessary, corrected using the following procedure and criteria:

(1) the relative retention indices from GC/MS analyses are used to help confirm peak

identification.

(2) the primary peak identification is determined by the data system, using the retention times based on reference calibration runs.

(3) the relative peak heights of the sample run ("fingerprint") are matched with the typical fingerprint seen in the past sample runs.

(4) the relative peak retention times of the sample run are compared with those of the reference runs; and

(5) any peak with reasonable doubt is labeled ‘Unidentified’.

6.8 After running an extremely "dirty" sample, the analyst may run a blank or flush the sampling system with zero nitrogen before proceeding to the next sample, as there may be sample carry-over.

6.9 All peaks identified as target compounds at or above the LOD are reported.

6.9.1 Target compounds (Ref. 9.1, Appendix 1) which coelute are reported as the major component as determined by the analysis of several samples by GC/MS or other methods.

6.9.2 An exception to this is m- and p-xylene. It has been stipulated that two-thirds of the coeluting peak is m-xylene and one-third is due to p-xylene. This ration of 2:1 was developed from GC/MS data and fuel profiles. This ratio is not used for peak identification and reporting of NMHC; the peak is reported as "m- & p-xylene". However, this ratio is used to calculate reactivity (Ref. 9.1, Parts E and G).

7 Calculations

7.1 A single-point calibration is performed daily with a NIST-traceable secondary calibration standard.

7.2 The hydrocarbon concentrations, in ppbC, are calculated by the data system using an external standard method.

$$\text{Sample Concentration} = \frac{\text{Sample Peak Area}}{\text{Response Factor}}$$

7.3 The response factor (RF) is calculated by:

$$RF = \frac{\text{Peak Area of calibration standard component}}{\text{Concentration of NIST-traceable calibration standard component}}$$

7.3.1 The light-end analysis is calibrated with propane.

7.3.2 The mid-range may be calibrated with either benzene or propane (Section 5.2).

8 Quality Control

8.1 A blank (pure nitrogen or helium) is run once daily before running the calibration standard, control standard, and samples. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed.

8.2 One run of the calibration standard is performed per day to generate the response factors needed for quantifying sample analyses.

8.3 One run of the quality control standard is performed daily.

8.3.1 A quality control chart is maintained for each monitored hydrocarbon compound in the control standard. The control charts, used on a daily basis, establish that the method is "in-control". The following describes how a typical control chart is constructed:

(1) obtain at least 20 daily control standard results;

(2) calculate the control standard mean concentration and standard deviation for the monitored hydrocarbon; and

(3) create a control chart for the monitored hydrocarbon by placing the dates on the x-axis and the concentrations on the y-axis. Establish an upper and lower warning limit at two standard deviations (2s) above and below the average concentration. Establish an upper and lower control limit at three standard deviations (3s) above and below the average concentration.

8.3.2 Measurements of all ten monitored hydrocarbon compounds contained in the control standard must be within the control limits ("in-control") before sample analysis may proceed. The results of all control monitored compounds are plotted on control charts. Values which exceed three standard deviations above or below the mean are considered to be "out of control". Values which exceed two standard deviations above or below the mean on two consecutive analysis days are also considered to be out of control on the second day. If one or more monitored hydrocarbon compounds are out of control, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards until the control standard criteria are met; when the QC criteria are met, sample analysis can continue. Figure 5 demonstrates a typical QC chart.

8.4 A duplicate analysis of one sample bag is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{\underline{\text{Difference between duplicate and original measurements X 100}}}{\text{Average of duplicate and original measurements}}$$

For each monitored hydrocarbon compound in the control standard, the allowable RPD depends on the average concentration of the duplicate runs, as shown in the following table (Ref. 9.1):

Average Measurement for Duplicate Runs	**Allowable RPD (%)**
1 to 10 times LOD	100
10 to 20 times LOD	30
20 to 50 times LOD	20
Greater than 50 times LOD	15

The results from duplicate analysis must meet the criteria above for all monitored hydrocarbon compounds in the control standard for Methods 1002 and 1003 (Ref.9.1). If the criteria are not met, the sample must be rerun. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed. Figure 6 shows a typical duplicate sample report.

8.6 A multipoint calibration to confirm instrument linearity is performed for the same ten monitored hydrocarbons as in the control standard (four in the light-end HC analysis, and six in the mid-range HC analysis). It is done for new instruments, after making instrument modifications which can affect linearity, and at least once per year. The multipoint consists of at least five concentrations, each above the maximum allowable LOD (20 ppbC), about evenly distributed over the range of expected sample concentration (from about 100 ppbC to about 10000 ppbC). Each concentration is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear to ensure the accuracy of the daily one-point calibration. Figure 7 illustrates a typical multipoint calibration.

8.7 The LOD for the same ten monitored hydrocarbons as in the control standard must be determined for new instruments, after making modifications which can affect linearity and/or sensitivity and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the expected LOD. The LOD is calculated using the following equation:

$$\text{LOD (ppbC)} = \frac{(|b| + (t \times s))}{m}$$

where

|b| = the absolute value of the y-intercept, area counts

m = the slope of the linear regression, area counts/ppbC

s = the standard deviation of at least five measurements of the lowest concentration standard, area counts

t = the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution, dimentionless

The number of degrees of freedom is equal to the number of runs (n) of the lowest concentration standard, minus one. An abbreviated t-table is (Ref.9.1):

Degrees of Freedom (n-1)	t-values
4	3.7
5	3.4
6	3.1
7	3.0

8.7.1 The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the estimated LOD. The maximum allowable LOD for each compound is 20 ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD.

8.7.2 All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported.

8.7.3 If the calculated laboratory LOD is less than the maximum allowable LOD, SLB may set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD. The current reporting limit is 15 ppbC. Figure 8 shows a typical LOD determination.

9.0 References

9.1 California Environmental Protection Agency, Air Resources Board, "California Non-methane Organic Gas Test Procedures", Part D (Method No. 1002 "Determination of C2 to C5 hydrocarbons in Automotive Source Samples by Gas Chromatography") and Part E (Method No. 1003 "Determination of C6 to C12 hydrocarbons in Automotive Source Samples by Gas Chromatography"), May 31, 1996.

9.2 Code of Federal Regulations, Title 40, Part 86.

9.3 Randy Bramston-Cook in Lotus Consulting monographs on "Speciation of Hydrocarbons in Vehicle Exhaust and Ambient Air" and "Quantitation of Hydrocarbons in Vehicle Exhaust and Ambient Air", 1996.

9.4 "Standard Test Method for C_1 Through C_5 Hydrocarbons in the Atmosphere by Gas Chromatography", ASTM Standards on Chromatography (1981).

9.5 U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method T93-15), EPA-600/4-89-017, Research Triangle Park, North Carolina, June 1989.

Table 2. Typical GC Operating Conditions

GC Parameters	Light-end GC	Mid-range GC	
		"Fast" Analysis	"Regular" Analysis
Column type	Alumina/KCl PLOT	DB-1 WCOT	DB-1 WCOT
Column size	0.32 mm ID, 50 m	0.18 mm ID, 40 m	0.32 mm ID, 60m
Helium carrier velocity	30 cm/sec at 200^{o}C	2 mL/min at 200^{o}C	30 cm/sec at 200^{o}C
Hydrogen gas flow(for FID)	25 mL/min	30 mL/min	30 mL/min
"Zero" air gas flow(for FID)	300 mL/min	300 mL/min	300 mL/min
Nitrogen make-up flow	30 mL/min	30 mL/min	30 mL/min
Auxiliary sample valve	150^{o}C	150^{o}C	150^{o}C
Precolumn temperature	40^{o}C	N/A	N/A
Column temperature	0^{o}C(hold 7 min)	-50^{o}C, hold	-50^{o}C, (hold 2 min)
	5^{o}C/min to 50^{o}C	8^{o}C/min to 170^{o}C	3^{o}C/min to 170^{o}C
	10^{o}C/min to 200^{o}C	50^{o}C/min to 250^{o}C	47^{o}C/min to 200^{o}C
	hold 15 min	End	30^{o}C/min to 250^{o}C
Cryotrap/Injector Program	-180^{o}C	-180^{o}C	-180^{o}C
	250^o/min to 200^{o}C	250^o/min to 200^{o}C	250^{o}C/min to 200^{o}C
	Hold for 28 min	hold for 28 min	hold for 70 min
Detector Temperature	250^{o}C	300^{o}C	300^{o}C
Detector Attenuation	8	8	8
Detector range	12	12	12
Total analysis time	30 min	35 min	90 min

```
Title        : Light-End GC#4L-7992-PC307
Run File     : C:\STAR\MODULE16\49C31157.RUN
Method File  : C:\STAR\GC4MR.MTH
Sample ID    : QA C3 AAL8623

Injection Date: 10-FEB-99 8:25 AM    Calculation Date: 10-FEB-99 8:42 AM

Operator    : LOS                    Detector Type: ADCB (10 Volts)
Workstation: AUTOGC4                 Bus Address   : 16
Instrument  : MR-GC4                 Sample Rate   : 10.00 Hz
Channel     : A = FID LE             Run Time      : 17.112 min

*********** Star Chromatography Workstation ******* Version 4.51 **************

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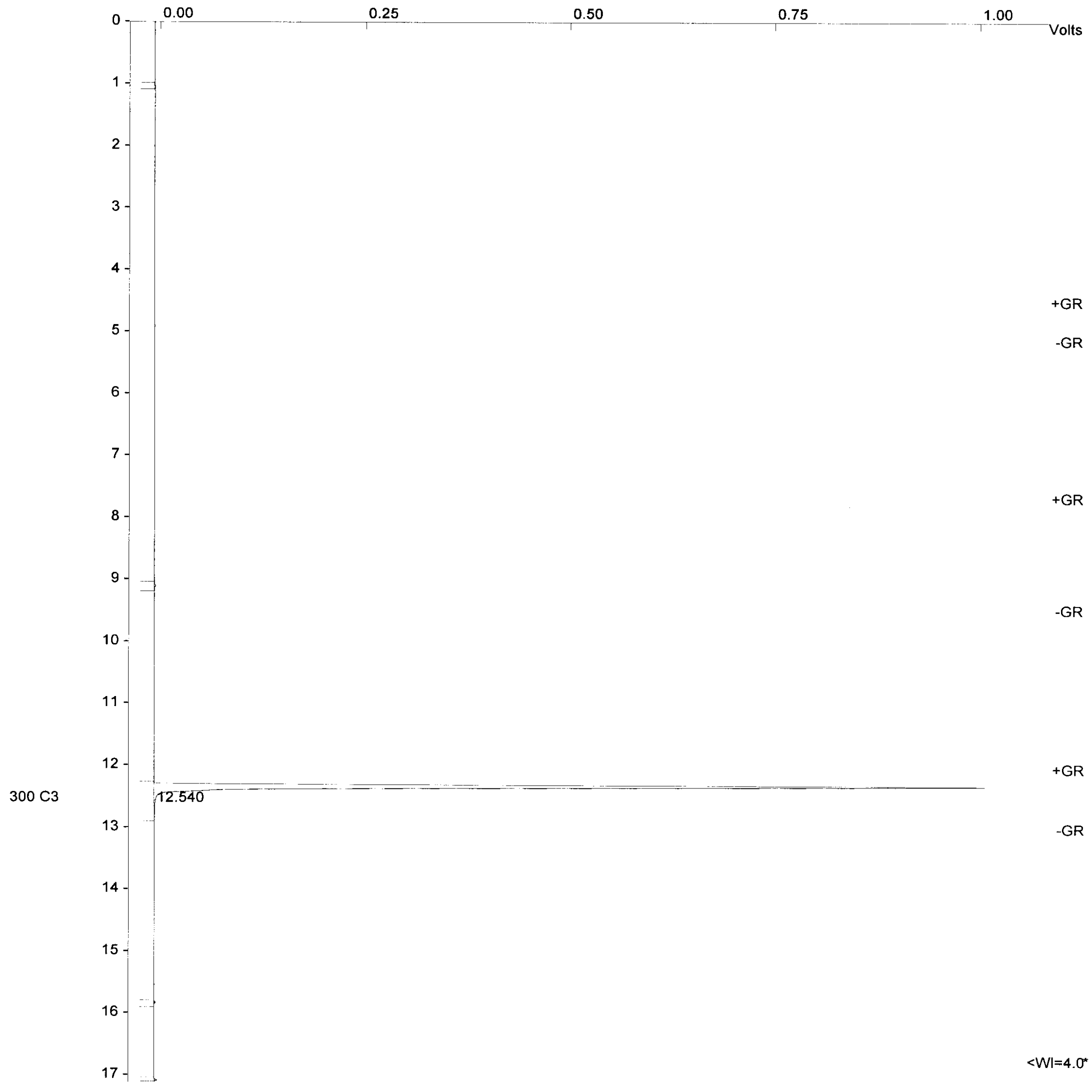

Figure 1

```
Title       : Mid-Range GC#4M-8020-PC307
Run File    : C:\STAR\MODULE16\49C31157.RUN
Method File : C:\STAR\GC4MR.MTH
Sample ID   : QA C3 AAL8623

Injection Date: 10-FEB-99 8:25 AM    Calculation Date: 10-FEB-99 8:42 AM

Operator    : LOS                    Detector Type: ADCB (10 Volts)
Workstation: AUTOGC4                 Bus Address  : 16
Instrument : MR-GC4                  Sample Rate  : 10.00 Hz
Channel     : B = FID MR             Run Time     : 17.112 min

*********** Star Chromatography Workstation ******* Version 4.51 **************

Chart Speed =    1.15 cm/min   Attenuation = 276          Zero Offset = 2%
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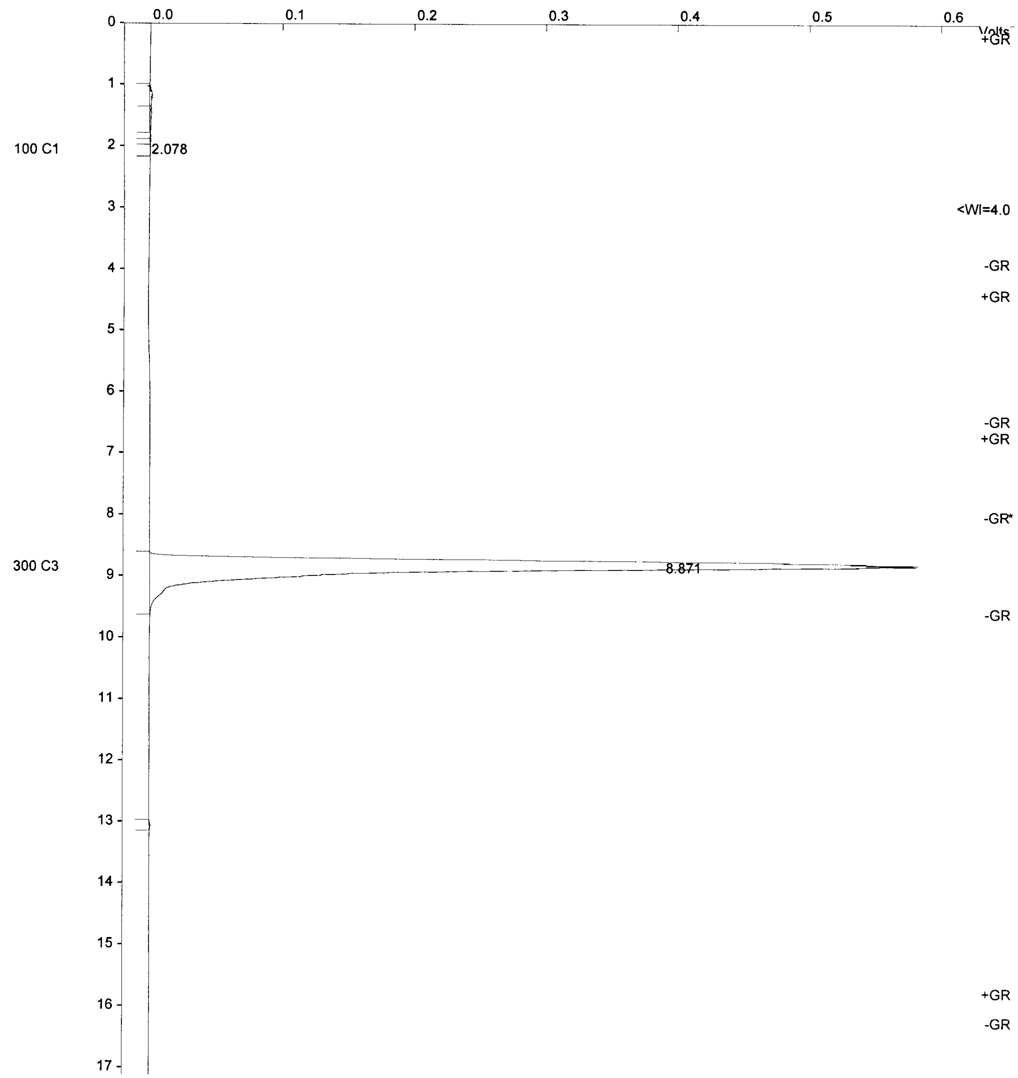

Figure 2

```
Title        : Light-End GC#4L-7992-PC307
Run File     : C:\STAR\MODULE16\49GH1106.RUN
Method File  : C:\STAR\GC4MR.MTH
Sample ID    : ssgh

Injection Date: 14-JAN-99 12:42 PM    Calculation Date: 14-JAN-99 1:58 PM

Operator    : LOS                    Detector Type: ADCB (10 Volts)
Workstation: AUTOGC4                 Bus Address  : 16
Instrument : MR-GC4                  Sample Rate  : 10.00 Hz
Channel     : A = FID LE             Run Time     : 76.003 min

*********** Star Chromatography Workstation ******* Version 4.51 **************

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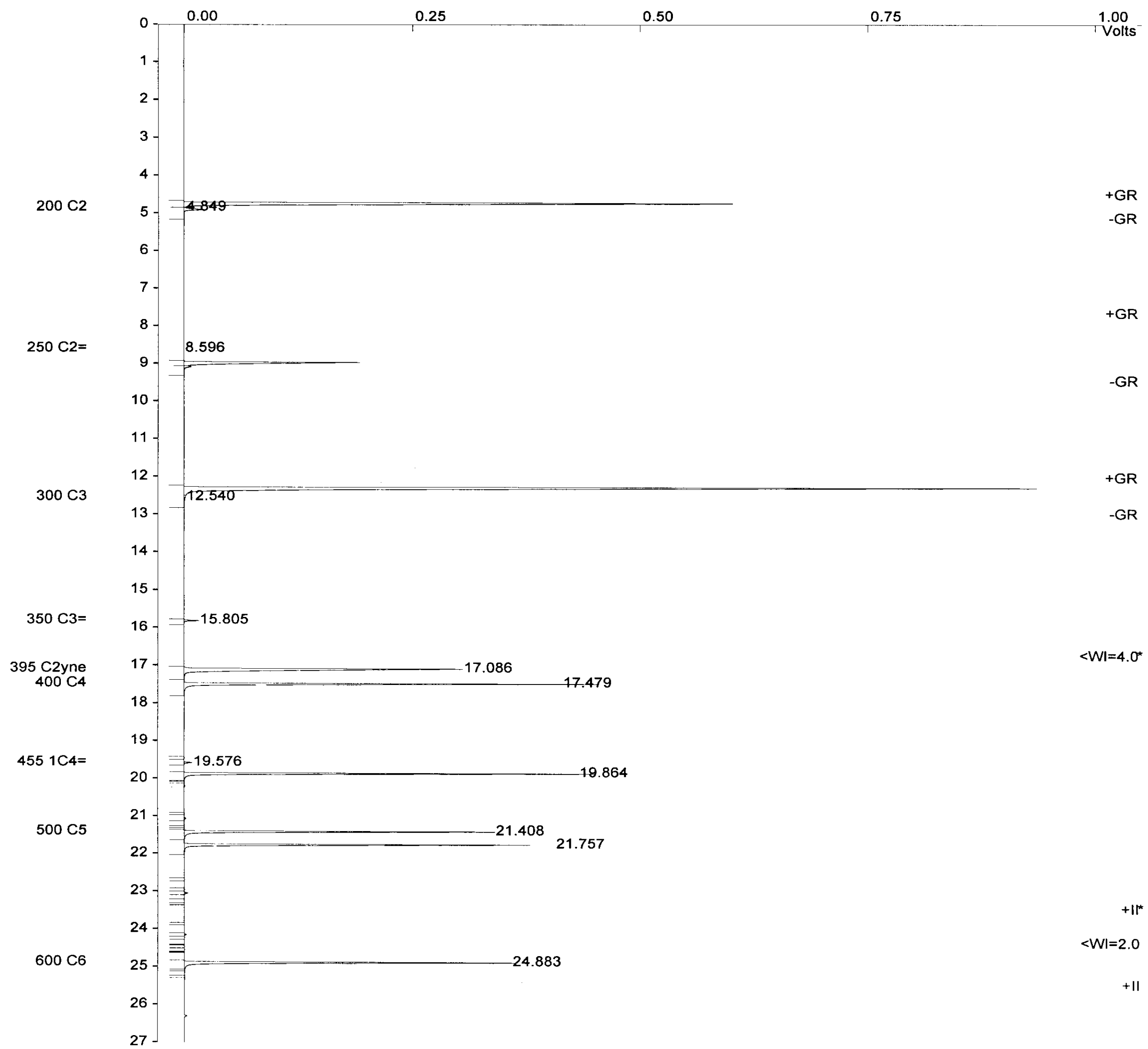

Figure 3

```
Title         : Mid-Range GC#4M-8020-PC307
Run File      : C:\STAR\MODULE16\49GH1106.RUN
Method File   : C:\STAR\GC4MR.MTH
Sample ID     : ssgh

Injection Date: 14-JAN-99 12:42 PM     Calculation Date: 14-JAN-99 1:58 PM

Operator    : LOS                     Detector Type: ADCB (10 Volts)
Workstation: AUTOGC4                  Bus Address  : 16
Instrument : MR-GC4                   Sample Rate  : 10.00 Hz
Channel     : B = FID MR              Run Time     : 76.003 min

*********** Star Chromatography Workstation ******* Version 4.51 **************

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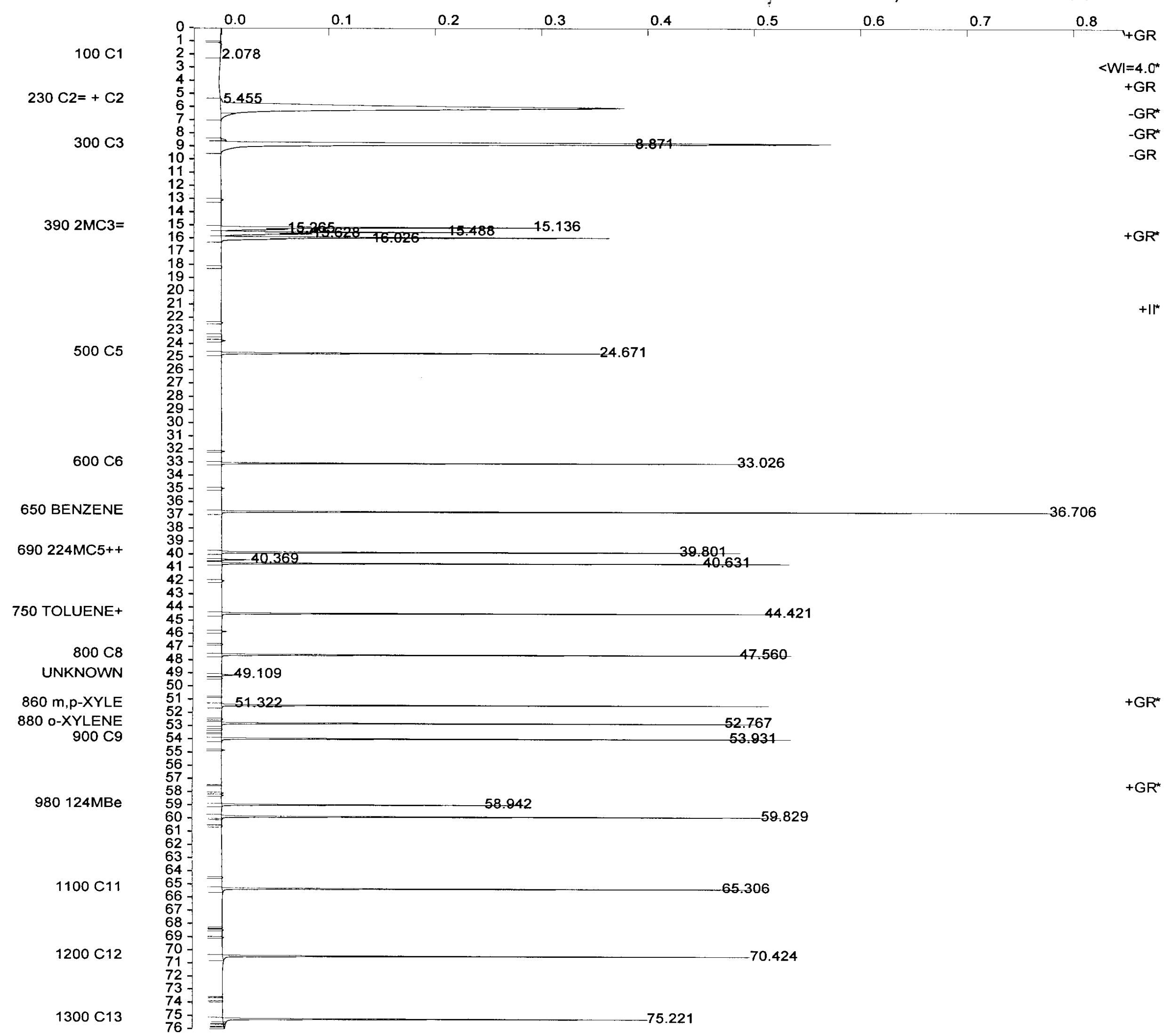

Figure 4

ETHANE

No. of Data	Date	**250 C2=**	STATUS
1	10/01/1998	614	OK
2	10/02/1998	621	OK
3	10/05/1998	617	OK
4	10/06/1998	611	OK
5	10/07/1998	615	OK
6	10/08/1998	621	OK
7	10/13/1998	614	OK
8	10/14/1998	610	OK
9	10/15/1998	606	OK
10	10/16/1998	618	OK
11	10/19/1998	606	OK
12	10/20/1998	609	OK
13	10/21/1998	590	WARNG
14	10/21/1998	600	OK
15	10/22/1998	607	OK
16	10/23/1998	618	OK
17	10/26/1998	617	OK
18	10/27/1998	612	OK
19	10/28/1998	622	OK
20	10/29/1998	611	OK
21	10/30/1998	612	OK
22	11/02/1998	608	OK
23	11/03/1998	603	OK
24	11/04/1998	598	OK
25	11/05/1998	612	OK
26	11/06/1998	626	OK
27	11/06/1998	618	OK
28	11/09/1998	612	OK
29	11/09/1998	605	OK
30	11/10/1998	617	OK
31	11/12/1998	610	OK
32	11/13/1998	614	OK
33	11/18/1998	590	WARNG
34	11/18/1998	611	OK
35	11/20/1998	599	OK
36	11/25/1998	602	OK
37	12/16/1998	626	OK
38	12/18/1998	620	OK
39	12/21/1998	619	OK
40	12/21/1998	621	OK

		-3 sigma	-2 sigma	+2 sigma	+3 sigma
MEAN	612				
SD	9.93	582	592	631	641
RSD	1.62%				

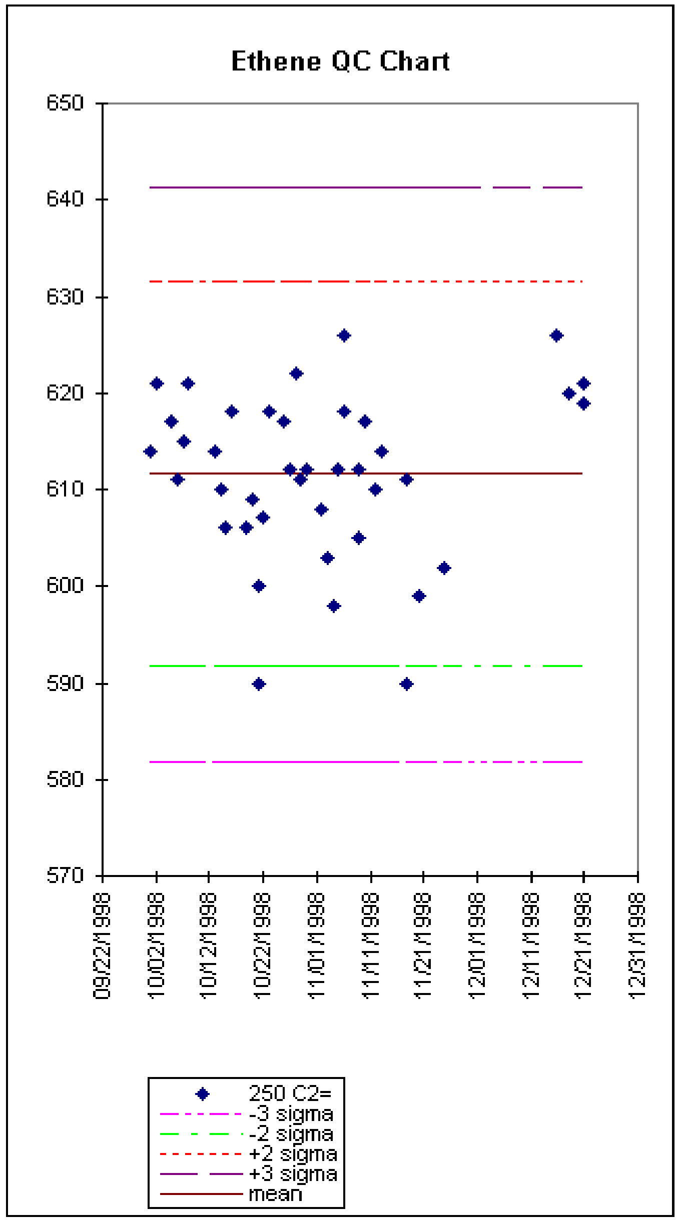

Figure 5

REPLICATES ANALYSIS

GC#4:7992 (LIGHT-END)

		ETHENE					PROPANE				
			LOD= 5.00					LOD= 5.00			
DATE	TEST #	RUN #1	RUN #2	%RPD	MAX. %RPD	STATUS	RUN #1	RUN #2	%RPD	MAX. %RPD	STATUS
10/01/1998	2C2A BG2	16	14	13	100	OK	26	19	31	100	OK
10/05/1998	PROPANE CYL	<L	<L	#VALUE!	#####	OK	137927	134531	2	15	OK
10/15/1998	10C24 BG1	650	648	0	15	OK	290	279	4	15	OK
10/16/1998	235C1 bag2	10842	10849	0	15	OK	140	125	11	20	OK
10/19/1998	235U1 bag2	22611	22650	0	15	OK	248	261	5	15	OK
10/20/1998	10C26 bag1	604	608	1	15	OK	101	100	1	20	OK
10/22/1998	13C25 bag1	1410	1380	2	15	OK	119	85	33	20	FAIL
10/23/1998	10C27 bag1	561	573	2	15	OK	56	50	11	30	OK
10/27/1998	10C28 bag3	13	13	0	100	OK	26	24	8	100	OK
10/28/1998	13C28 bag3	51	55	8	30	OK	72	80	11	30	OK
10/29/1998	13C29 bag3	128	127	1	20	OK	57	56	2	30	OK
10/30/1998	13C30 bag1	1623	1613	1	15	OK	42	43	2	100	OK
11/03/1998	10C32 bag1	557	563	1	15	OK	65	70	7	30	OK
11/04/1998	10C33 bag1	559	555	1	15	OK	91	93	2	30	OK
11/05/1998	6C1 bag1	676	678	0	15	OK	259	299	14	15	OK
11/06/1998	5C1 bag1	1845	1830	1	15	OK	226	222	2	20	OK
11/10/1998	6C3 bag1	738	743	1	15	OK	42	44	5	100	OK
11/20/1998	6C4 bag1	622	623	0	15	OK	34	38	11	100	OK
12/16/1998	262C1 BG2	15390	14703	5	15	OK	315	289	9	15	OK

Figure 6

SUMARY RESULTS OF LINEARITY CHECK

Period: 03/25/1996
Gas Chromatograph: No. 6 (MR=8018)

HYDROCARBON: HEXANE — R= 0.9978, M= 138.50

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	42168	274
NIST STD..AAL111183(w w)	0.1	3	140478	888
NIST STD..AAL111183(w w)	0.2	3	305748	1776
NIST STD..AAL111183(w w)	0.4	3	544257	3552
NIST STD..AAL111183(w w)	0.7	3	914379	6216
NIST STD..AAL111183(w w)	0.9	3	1170017	7992
NIST STD..AAL111183(w w)	Undiluted	6	1211005	8880

HYDROCARBON: BENEZENE — R= 0.9987, M= 140.74

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	41058	258
NIST STD..AAL111183(w w)	0.1	3	146957	1002
NIST STD..AAL111183(w w)	0.2	3	342511	2004
NIST STD..AAL111183(w w)	0.4	3	594379	4008
NIST STD..AAL111183(w w)	0.7	3	1025474	7014
NIST STD..AAL111183(w w)	0.9	3	1322584	9018
NIST STD..AAL111183(w w)	Undiluted	6	1394944	10020

HYDROCARBON: TOLUENE — R= 0.9563, M= 157.96

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	39888	218
NIST STD..AAL111183(w w)	0.1	3	153211	1008
NIST STD..AAL111183(w w)	0.2	3	376368	2016
NIST STD..AAL111183(w w)	0.4	3	627248	4032
NIST STD..AAL111183(w w)	0.7	3	1085002	7058
NIST STD..AAL111183(w w)	0.9	3	1389105	6072
NIST STD..AAL111183(w w)	Undiluted	6	1500967	10080

HYDROCARBON: OCTANE — R= 0.9990, M= 149.20

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	40931	278
NIST STD..AAL111183(w w)	0.1	3	153096	1000
NIST STD..AAL111183(w w)	0.2	3	355672	2000
NIST STD..AAL111183(w w)	0.4	3	621510	4000
NIST STD..AAL111183(w w)	0.7	3	1087118	7000
NIST STD..AAL111183(w w)	0.9	3	1381968	9000
NIST STD..AAL111183(w w)	Undiluted	6	1477929	10000

HYDROCARBON: XYLENE — R= 0.9986, M= 151.05

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	39835	253
NIST STD..AAL111183(w w)	0.1	3	149961	992
NIST STD..AAL111183(w w)	0.2	3	384404	1984
NIST STD..AAL111183(w w)	0.4	3	596373	3968
NIST STD..AAL111183(w w)	0.7	3	1058690	6944
NIST STD..AAL111183(w w)	0.9	3	1381909	8928
NIST STD..AAL111183(w w)	Undiluted	6	1512694	9920

HYDROCARBON: DECANE — R= 0.9989, M= 146.15

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	Undiluted	5	39689	242
NIST STD..AAL111183(w w)	0.1	3	138756	936
NIST STD..AAL111183(w w)	0.2	3	338353	1872
NIST STD..AAL111183(w w)	0.4	3	540051	3744
NIST STD..AAL111183(w w)	0.7	3	990061	6662
NIST STD..AAL111183(w w)	0.9	3	1266139	8424
NIST STD..AAL111183(w w)	Undiluted	6	1370613	9360

Figure 7

SUMARY RESULTS OF LOD CHECK

Period: 03/25/1996
Gas Chromatograph: No. 6 (MR=8018)

HYDROCARBON: HEXANE — LOD= 5.77 ppbc — R= 0.9884, M= 145.51

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	4396	27
NIST STD..AAL10318(v v)	0.2	3	8574	55
NIST STD..AAL10318(v v)	0.5	3	21375	137
NIST STD..AAL10318(v v)	0.8	3	28397	219
NIST STD..AAL10318(v v)	Undiluted	3	42736	274

HYDROCARBON: BENZENE — LOD= 2.7 ppbc — R= 0.9847, M= 151.32

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	4247	26
NIST STD..AAL10318(v v)	0.2	3	8073	52
NIST STD..AAL10318(v v)	0.5	3	20407	129
NIST STD..AAL10318(v v)	0.8	3	26716	205
NIST STD..AAL10318(v v)	Undiluted	3	41950	258

HYDROCARBON: TOLUENE — LOD= 1.9 ppbc — R= 0.9876, M= 188.33

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	41.62	22
NIST STD..AAL10318(v v)	0.2	3	7646	44
NIST STD..AAL10318(v v)	0.5	3	19789	109
NIST STD..AAL10318(v v)	0.8	3	26792	174
NIST STD..AAL10318(v v)	Undiluted	3	40478	218

HYDROCARBON: OCTANE — LOD= 2.21 ppbc — R= 0.9895, M= 139.87

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	4254	28
NIST STD..AAL10318(v v)	0.2	3	8144	56
NIST STD..AAL10318(v v)	0.5	3	20143	139
NIST STD..AAL10318(v v)	0.8	3	27617	222
NIST STD..AAL10318(v v)	Undiluted	3	41409	278

HYDROCARBON: XYLENE — LOD= 2.73 ppbc — R= 0.9829, M= 148.02

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	4295	25
NIST STD..AAL10318(v v)	0.2	3	7579	51
NIST STD..AAL10318(v v)	0.5	3	19235	126
NIST STD..AAL10318(v v)	0.8	3	25572	202
NIST STD..AAL10318(v v)	Undiluted	3	40529	253

HYDROCARBON: DECANE — LOD= 4.43 ppbc — R= 0.9846, M= 156.06

Standard ID	Dilution Factor	Number of Runs	Average Area Count	ppmC W/R to List Values
NIST STD..AAL10318(v v)	0.1	5	4620	24
NIST STD..AAL10318(v v)	0.2	3	8282	48
NIST STD..AAL10318(v v)	0.5	3	18427	121
NIST STD..AAL10318(v v)	0.8	3	26620	194
NIST STD..AAL10318(v v)	Undiluted	3	41190	242

Figure 8